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TO: John Sanders, Ph.D., Chief
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FROM: Jeff Cook, Chief
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DATE: September 8, 2004

SUBJECT: FINAL PROTOCOL FOR THE 2004 FIELD APPLICATION AIR MONITORING FOR CHLOROPICRIN

Attached is the final "Protocol for Air Monitoring Around a Field Application of Chloropicrin - 2004". We received your August 20, 2004 comments on the draft protocol and have made the changes you recommended.

If you or your staff have questions or need further information, please contact me at 322-3726 or Kevin Mongar at 322-2449.

Separate Attachment

cc: Randy Segawa, DPR (w/Attachment)
Pam Wofford, DPR (w/Attachment)
Kevin Mongar, MLD (w/Attachment)

State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

Protocol for Air Monitoring Around a Field Application of Chloropicrin 2004

Prepared by
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Quality Management Branch
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Date: August 27, 2004

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This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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Around a Field Application
of Chloropicrin
2004

I. Introduction

At the request of the California Department of Pesticide Regulation (DPR) (October 17, 2003 Memorandum, Helliker to Lloyd), the Air Resources Board (ARB) staff will measure airborne concentrations of the pesticide chloropicrin around a field application. The monitoring test is tentatively scheduled to be conducted in late summer or fall 2004. This monitoring will be done to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) which requires the ARB "to document the level of airborne emissions...of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR.

The sampling and analysis will follow the quality assurance guidelines described in the "Quality Assurance Plan for Pesticide Air Monitoring" (May 11, 1999 version).

The sampling and analysis will follow the procedures outlined in this protocol as well as the procedures described in Attachment I, "Standard Operating Procedure for Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector" (July 14, 2004 Version).

II. Sampling

Chloropicrin samples will be collected on XAD-4 resin sampling cartridges. For chloropicrin, the tubes are 8 mm x 140 mm, XAD-4, with 400 mg in the primary section, and 200 mg in the secondary section (SKC special order). Sample collection is at a flow rate of 100 standard cubic centimeters per minute (sccpm). Subsequent to sampling, the tubes are capped, labeled, placed in a culture tube, and stored and transported in an insulated container with dry ice. The samples are transported by vehicle to the ARB laboratory in Sacramento. DPR recommends a target 24-hour estimated quantitation limit (EQL) for chloropicrin of 0.1 ug/m^3.

Caution should be used during field monitoring, transportation, storage, and lab analysis to minimize exposure of samples to sunlight in order to prevent photo degradation of chloropicrin.

Each sample train consists of an adsorbent tube, Teflon fittings and tubing, rain/sun shield, needle valve, train support, and a 12 volt DC vacuum pump (see Figure 1). Each tube is prepared in the field by breaking off each sealed glass end and immediately inserting the tube into the fitting. The tubes are oriented in the sample

train with a small arrow printed on the side of each tube indicating the direction of flow. The flow rates will be set using a calibrated digital mass flow meter (MFM) before the start of each sampling period. The MFM used for the chloropicrin samplers has a range of 0-200 sccpm. The mass flow meter has been calibrated to standard conditions (1 atm and 25 °C). The flow rate is also checked and recorded, using the MFM, at the end of each sampling period. Any change in flow rates will be recorded in the field logbook (see Attachment III). The pesticide sampling procedures for adsorbent tubes are included as Attachment II. The sampling schedule consists of samples collected during daylight and overnight periods as shown below in Table 1.

Table 1
Application Sampling Schedule

Sample period begins	**Sample duration**
Background (pre-application)	Daytime/Overnight (two samples) 24 hours total
During application and post –application	Start of application until 1 hour before sunset (or until end of application if after sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)

The application monitoring study will be conducted at the location and under the conditions described in Table 2.

Table 2
Application Information

Location:	To be Determined
Field Size:	Largest field that can be fumigated in 1 day
Product Applied:	Metapicrin, 100% chloropicrin (by weight)
Type of Application:	Drip (prefer untarped)
Commodity:	To be Determined
Application Rate:	Maximum label rate (100lbs/acre or higher)
Grower/Applicator:	To be Determined

An attempt will be made to select a study site where there have been no chloropicrin applications to adjacent fields for at least 5 days prior to the test application and no applications anticipated to adjacent fields for three days following the test application.

A minimum of 8 samplers will be positioned, one on each side of the field and one at each corner. A ninth replicate sampler will be collocated at one downwind site. Samplers should be positioned 20 meters from the field edge. Site conditions will dictate the exact placement of samplers.

In regard to field data, the monitoring report will include: 1) a record of the positions of the monitoring equipment with respect to the field, 2) the application start location, 3) the direction of crop rows 4) how the field was divided to treat if over several days, 5) a drawing of the monitoring sites showing the precise location of the meteorological equipment, trees, buildings and other obstacles, 6) meteorological data collected at a minimum of 5-minute intervals including wind speed and direction, humidity, and air temperature and comments regarding degree of cloud cover, 7) the elevation of each sampling station with respect to the field, and the orientation of the field with respect to North (identified as either true or magnetic North), and 8) the start and end time of the application. In addition, any materials and procedures used to tarp the field will be documented.

III. Analysis

The sampling and analysis method and validation results for the sampling and analysis of chloropicrin are included as Attachment I. The chloropicrin method will consist of sampling with XAD-4 resin cartridges along with GC analysis with mass selective detector. The method detection limit (MDL) and estimated quantitation limit (EQL) for chloropicrin are 3.96 ng/sample and 19.8 ng/sample, respectively. For a 24-hour sample at 100 sccpm, the MDL and EQL would be 27.5 ng/m^3 and 138 ng/m^3, respectively. The DPR target EQL is 100 ng/m^3. The analyses will be performed by the ARB laboratory in Sacramento.

IV. Field Quality Assurance

Field Quality Control for the application monitoring will include the following:

1) Four field spikes will be obtained by sampling ambient air at the application monitoring site for 24 hours (daytime/overnight). The field spikes will be obtained by sampling ambient air during the background monitoring (i.e., collocated with a background sample at the same environmental and experimental conditions). The spike levels for chloropicrin in the adsorbent tube samples have not yet been determined.

2) Four trip spikes will be prepared at the same level as the field spikes. The trip spikes will be labeled, recorded on the field log-sheet, and transported along with the field spikes and application samples.

3) Four lab spikes will be prepared at the same level as the field and trip spikes. The lab spikes will remain in the laboratory freezer and will be extracted and analyzed along with the field and trip spikes.

4) Collocated (replicate) samples will be taken for all sampling periods (except the background period) at one sampling location (downwind).

5) A trip blank will be obtained, labeled, recorded on the field log-sheet, and transported along with the field spikes and application samples.

V. Sample Labeling

Samples will be labeled using the following format:

Location-Chemical-Sampling Period-Type of Sample

Where (as an example):
Location is designated as north 1, 2 or 3 (N1, N2, N3), west (W), south 1, 2 or 3 (S1, S2, S3), and east (E). These designations can be revised as necessary depending on the configuration of the field.

Chemical is designated as C for chloropicrin.

Sampling period is designated as B (for background) or 1 through 6.

The type of sample is designated as S (sample), C (collocated), TB (trip blank), TS (trip spike), and FS (field spike).

Examples:	S2-C-B-S	(South2, Chloropicrin, background, sample)
	S2-C-B-FS	(South2, Chloropicrin, background, field spike)
	S2-C-1-S	(South2, Chloropicrin, sampling period 1, sample)
	S2-C-1-C	(South2, Chloropicrin, sampling period 1, collocated)

VI. Personnel

ARB sampling personnel will consist of staff from the ARB's Air Quality Surveillance Branch.

VII. Safety Recommendations

Refer to Attachment IV for general information on and toxicology of chloropicrin gas fumigant. The DPR's Monitoring Recommendations include the following safety recommendations for chloropicrin.

> "The chloropicrin product labels warn that chloropicrin is a poisonous liquid and vapor and is readily identifiable by smell. Inhalation of vapors may be fatal and exposures to low concentrations of vapor will cause irritation of the eyes, nose, and throat. Exposure to high concentrations or for a prolonged period of time may cause painful irritation to the eyes or temporary blindness. Contact with the liquid will cause chemical burns to the skin or eyes and is harmful or fatal if swallowed.
>
> The acceptable air concentration for persons exposed to chloropicrin is 0.1 ppm. If air concentrations exceed 0.1 ppm, an air purifying respirator must be worn. The highest concentrations of chloropicrin at 20 m from the field should not exceed 0.05 to 0.08 ppm. The label states that the applicator and other handlers must wear: loose fitting, long –sleeve shirt and long pants, shoes and socks, and full-face shield or safety glasses with brow and temple shields. Monitoring personnel should refer to the label of the product used and should use proper protective equipment to prevent exposure to the dust, vapors, or spray mist."

MANIFOLD SAMPLER

01/29/02

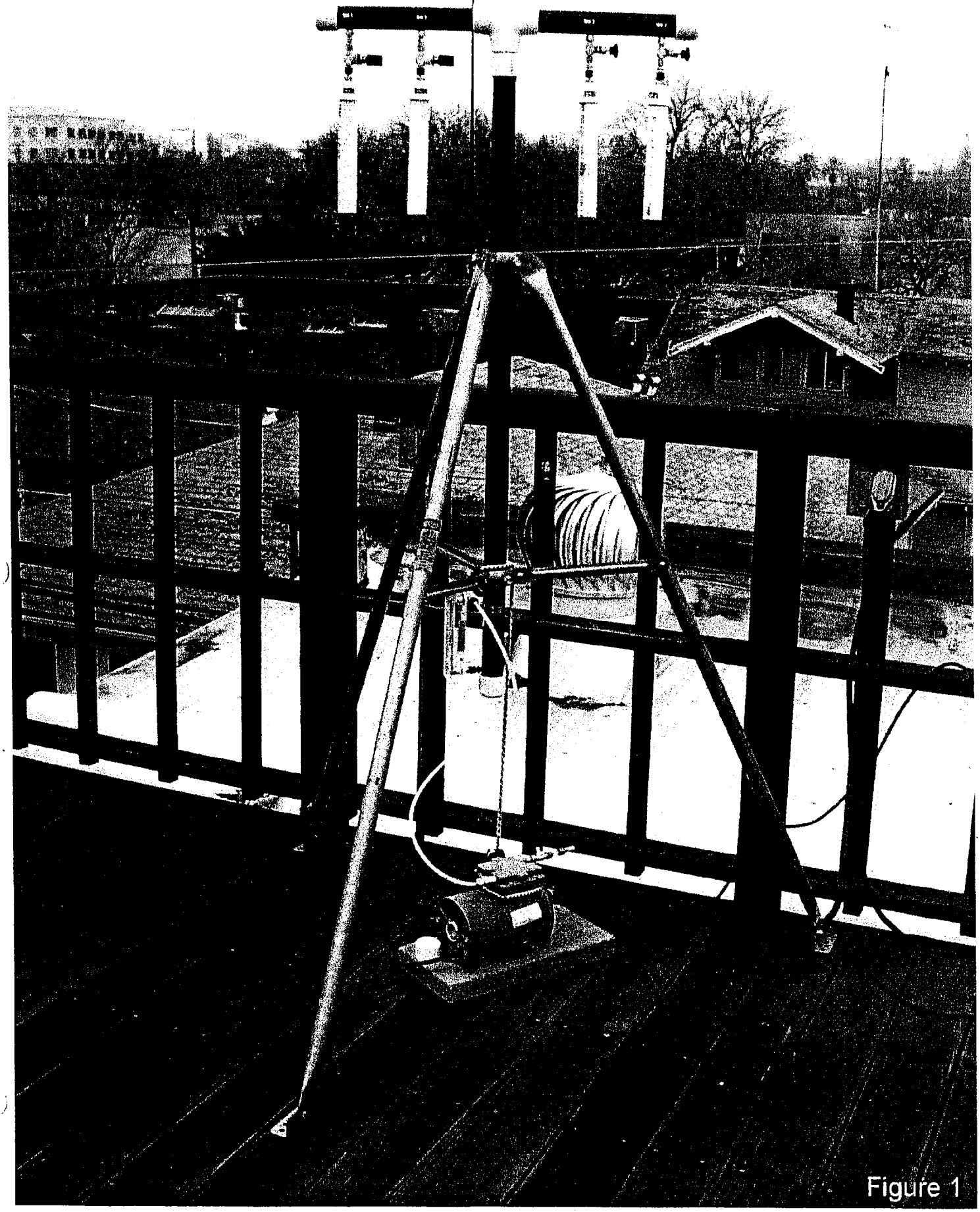

Figure 1

Attachment I

Standard Operating Procedure, Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector

California Environmental Protection Agency

Air Resources Board

Standard Operating Procedure for
Sampling and Analysis of Trichloronitromethane
(Chloropicrin) in Application and Ambient Air using Gas
Chromatography/Mass Selective Detector

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

Revision 3
7/14/04

Approved by:

Russell Grace, Manager
Special Analysis Section

1. SCOPE

The current method is for the analysis of trichloronitromethane (TCNM) using a gas chromatograph/mass selective detector. The procedure is for the analysis of application and ambient air monitoring of TCNM using XAD-4 resin tubes. The Department of Pesticide Regulation (DPR) asked the Air Resources Board (ARB) to analyze for TCNM during agricultural/structural application and ambient monitoring with an estimated quantitation limit of 0.1 $\mu g/m^3$.

2. SUMMARY OF METHOD

Resin tubes, XAD-4, are placed on the sampler for 24 hours at a flowrate of 0.1 liters per minute (LPM or 100 mLPM). The samples are stored in an ice chest or refrigerator until extracted with 3.0 ml of dichloromethane (DCM). A gas chromatograph with a mass selective detector in the selected ion monitoring (SIM) mode is used for analysis.

3. INTERFERENCES/LIMITATIONS

Interferences may be caused by contaminants in solvents, reagents, glassware and other processing apparatus that can lead to discrete artifacts or elevated baselines. A method blank, including both solvent and resin, must be analyzed with each batch of samples to detect any possible interferences.

4. EQUIPMENT AND CONDITIONS

A. INSTRUMENTATION:

Hewlett-Packard 6890 Series gas chromatograph
Hewlett-Packard 5973 Network mass selective detector
Hewlett-Packard 6890 Enhanced Parameters ALS

MS Transfer line: 280°C
Injector: 180°C, Splitless, Liner 4 mm straight liner with glass wool
Column: Restek Rtx-200, 60 meter, 320 µm i.d., 1.5 µm film thickness, or equivalent

GC Temperature Program: Oven initial 40°C, hold 1 min. Ramp to 160°C @ 20°C/min., ramp to 240°C @ 50°C/min., hold 3.0 min.
Retention time: TCNM 11.60 min.

Splitter open @ 1.0 min.
Flows: Column: He, 1.6 ml/min, 9.1psi. (velocity: 32cm/sec)
Splitter: 50 ml/min.

Mass Spectrometer: Electron Ionization
Selective Ion Monitoring: trichloronitromethane: 117 (quant. ion 100%), 119 (qual. ion 98%); Tuning: PFTBA on masses 69, 219, 502

B. Auxiliary Apparatus

1. Precleaned vials, 8 ml capacity with teflon caps
2. Silanized Glasswool
3. Disposable syringes, 3 ml
4. Sonicator
5. GC vials with septum caps

C. Reagents

1. Dichloromethane, Pesticide grade or better
2. Trichloronitromethane, Chem Service PS-4, 98.8%
3. XAD-4 resin sorbent tubes, 400/200mg, SKC, Fullerton, CA

5. ANALYSIS OF SAMPLES

1. A daily manual tune shall be performed using PFTBA. The instrument is tuned using masses: 69, 219, 502. The criterion for the tune are the peak widths at ½ the peak height, 0.60 ± 0.05, and the criteria for relative abundance: 69:100%, 219:90-120%, and 502: 5-12%.

2. It is necessary to analyze a solvent blank with each batch of samples. The blank must be free of interferences. A solvent blank must be analyzed after any sample that may result in possible carry-over contamination.

3. A five or six-point calibration curve shall be analyzed with each batch of samples. The calibration will be 5.0-150.0 ng/mL for both the application and ambient studies.

4. A calibration check sample (20 ng/ml) is run after the calibration, after every ten samples and at the end of the sample batch. The value of the calibration check must be within $\pm 3\sigma$ (the standard deviation) or ±10% of the expected value whichever is greater. If the calibration check is outside this limit, then those samples in the batch after this calibration check need to be reanalyzed.

5. With each batch of samples analyzed, a laboratory blank and a laboratory control spike will be run concurrently. A laboratory blank is XAD-4 extracted and analyzed the same way as the samples. A laboratory control spike is XAD-4 spiked with a known amount of standard. The laboratory control

sample is extracted and analyzed the same way as the samples. Laboratory control samples should have recoveries that are greater than or equal to 70% of the theoretical spiked value.

6. Score and snap the sample resin tube, transfer the front bed of the resin tube into an 8-ml vial. (Save the back-up bed for future analysis if necessary.) Rinse the tube with 3.0 ml of DCM into the extraction vial. Cap and place the vial in the sonicator for one hour.

7. Filter the samples using silanized glasswool plugged 3-ml syringe directly into a GC vial and cap securely.

8. The atmospheric concentration is calculated according to:

   Conc (ng/m^3) = Extract Conc (ng/ml) X 3 ml / Air Volume Sampled (m^3)

6. QUALITY ASSURANCE

A. Instrument Reproducibility

The reproducibility of the instrument and analytical method was established by analyzing five (5) 1.0 µl injections of trichloronitromethane standard at three concentrations (low, mid, and high). The low, mid and high concentrations were 5, 20 and 50 ng/ml, respectively.

B. Calibration

A five or six-point calibration curve is made ranging from 5.0 ng/ml to 150.0 ng/ml.

C. Calibration Check

A calibration check sample is run after the calibration, after every ten samples and at the end of the sample batch to verify the system is in calibration. The value of the check must be within $\pm 3\sigma$ (the standard deviation) or $\pm 10\%$ of the expected value whichever is greater. If the calibration check is outside the limit, then those samples in the batch after this calibration check, need to be reanalyzed.

D. Minimum Detection Limit

The detection limit is based on US EPA MDL calculation. Using the analysis of seven (7) replicates of a low-level matrix spike, the method detection limit (MDL) and the estimated quantitation limit (EQL) for trichloronitromethane is calculated

by: MDL = 3.14*(std dev values), where std dev = the standard deviation of the concentration calculated for the seven replicate spikes. For TCNM the MDL is 3.96 ng/sample (1.32 ng/mL). EQL, defined as 5*MDL, is 19.8 ng/sample (6.60 ng/mL) based on a 3.0 ml extraction volume. Results are reported to three significant figures. Results below EQL but above the MDL are reported as DET (detected) and results less than the MDL are reported as ND (nondetect) or <MDL.

E. Collection and Extraction Efficiency (Recovery)

Trichloronitromethane at a low and high level are spiked on XAD-4 tubes (three at each concentration). The spiked tubes are placed on field samplers with airflows of 100 mLpm for 24 hours. The samples are extracted with DCM and prepared as described in section 5, #6-7. The average percent recovery of trichloronitromethane should be $\pm$ 20% of the expected value. The recoveries both for the low and high levels are greater than 80.0%.

F. Storage Stability

Storage stability was set up for a four-week study. Three (3) XAD-4 tubes each were spiked at the low and high-end concentrations. The tubes were stored in the freezer until analyzed. At the low-end concentrations (5 ng/ml), the recovery for the three spikes averaged 106.8 percent, ranging from 103.68 to 113.68 percent. The average percent recovery peaked after fourteen days and was at the lowest after 28 days. At the high end (50 ng/ml), the recovery for the three spikes averaged 90.24 percent, ranging from 88.90 to 92.00 percent. The average percent recovery peaked at fourteen days and was at the lowest at twenty days.

G. Breakthrough

The most recent study for ambient monitoring for 24 hours required a low sample flow rate to meet the requested EQL. A new breakthrough analysis study was conducted. The flow rates tested were 1.0, 0.5, 0.2 and 0.1 Lpm. To meet the EQL and minimize breakthrough possibility, the flow rate for the field sampling was set at 100 mLpm.

H. Safety

This procedure does not address all of the safety concerns associated with chemical analysis. It is the responsibility of the analyst to establish appropriate safety and health practices. For hazard information and guidance refer to the material safety data sheets (MSDS) of any chemicals used in this procedure.

Attachment II

Application Sampling Procedures
For Adsorbent Tubes

Application Sampling Procedures
For Adsorbent Tubes

Overview:

-Collect samples, according to the schedule in Table 1 of this protocol.

-Collect 4 background samples, from each corner sampling position.

-Collocate 1 field spike with each of the 4 background samples.

-Collect a collocated sample from one site (the downwind site) for all sampling periods (except the background period).

-Submit 1 trip blank.

--All samples are stored either in an ice-chest on dry ice or in a freezer.

-The field log sheet is filled out as the sampling is conducted. All QA samples (field and trip spikes and trip blanks) must be logged onto the log sheet.

-The chain of custody (COC) forms are filled out prior to sample transfer; the originals are transferred with the samples; make and retain copies if desired.

Sampling Procedure:

Materials that will be needed to conduct the sampling include:

-Clip board with log sheets
-pencils/pens
-sample labels
-sample cartridges
-end caps
-plastic test tubes
-zip-lock bags
-0 to 200 sccpm mass flow meter (MFM) with battery
-ice chest
-dry ice

Figure out the route for sampling the 8 locations and try to keep this the same throughout the study.

Preparation and Set-up

On the way to the study site, plug the MFM into the battery. It takes the MFMs about 10 minutes to warm up before they can be used. Leave the MFM plugged in until the last sample is taken; unplug when not in use to minimize drop in battery charge. Recharge the batteries once per week to be on the safe side.

Securely attach one adsorbent sample cartridge to the sampling tree. MAKE SURE THE ARROW ON THE CARTRIDGE IS POINTING TOWARDS THE SAMPLE LINE.

Using the 0-200sccpm MFM set the flow rate exactly to 100 sccpm. Use the MFM calibration linear regression equation to set the flow rate.

Make sure that the rain/sun cover is pulled down over the sample tube.

Fill out the log sheet, including: log #, start date, time, start counter reading, MFM Serial #, any comments and the weather conditions.

Sample collection and Shipment
Measure (do not re-set) the flow rates at the end of the sampling period with the MFM; record the end data on the log sheet.

Remove the sample cartridge and cap the ends. Attach the sample label like a flag on the secondary end of the tube. Make sure that the label does not cover the glass wool separating the primary and secondary beds in the cartridge.

Place the cartridge in the plastic test tube shipping container.

Place all the samples for each period in a zip-lock freezer storage bag and place on dry ice in a cooler.

Collect a trip blank (TB) by breaking the ends off of a tube, capping and labeling as usual and storing along with the rest of the samples. Log the TB into the log sheet.

Attachment III

Field Log Sheet

CARTRIDGE FIELD LOG SHEET

Project: Chloropicrin Fumigation Air Monitoring

Project #: P-04-003 Start Flow Set: 100 ±2ccm End Flow Criteria: 100 ccm ±25%

Log #	Sample Name	Sampler ID Number	Date & Time		Counter		Mass Flow Meter Display		Corrected Average Flow	Comment Number	Weather K,P,C,F&R		Initials	
			Start	End	Start	End	Start	End			Start	End	Start	End

MFM Used #: _____ **Slope:** _____ **Intercept:** _____

Weather Codes: K = Clear, P = Partly Cloudy, C = ≥67% Cloudy, F = Fog, and R = Rain (any)

Attachment IV

Chloropicrin "Information Profile"

EXTOXNET

Extension Toxicology Network

Pesticide Information Profiles

A Pesticide Information Project of Cooperative Extension Offices of Cornell University, Oregon State University, the University of Idaho, and the University of California at Davis and the Institute for Environmental Toxicology, Michigan State University. Major support and funding was provided by the USDA/Extension Service/National Agricultural Pesticide Impact Assessment Program.

EXTOXNET primary files maintained and archived at Oregon State University

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CHLOROPICRIN

TRADE OR OTHER NAMES: Some trade names for products containing chloropicrin include "Chlor-O-Pic," "Metapicrin" "Timberfume" and "Tri-Clor." A partial list of trade names for chloropicrin mixtures with methyl bromide includes "Tri-Con," "Terr-O-Gas," "Preplant Soil Fumigant" and "Pic-Brom." Chloropicrin mixtures with 1,3-Dichloropropene include "Telone C-17," "Tri-Form" and "Pic-Clor."

REGULATORY STATUS: Chloropicrin is currently undergoing USEPA FIFRA reregistration. It is a Class I toxicity, Restricted Use Pesticide (RUP), labeled with the signal word "Danger" (231). The U.S. Department of Transportation (DOT) proper shipping name is "Chloropicrin, 6.1, UN 1580, PGI, Poison Inhalation Hazard, Hazard Zone B." The Emergency Response Guide (ERG) number is 56. NFPA designations are 4-Health, 0-Fire, 3-Reactivity. Chloropicrin is not listed under the EPA Clean Air Act, EPA Clean Water Act or the EPA Marine Pollutant List (258). A tolerance is not required for preplant soil fumigation uses of chloropicrin.

INTRODUCTION: Chloropicrin is a clear, colorless, oily liquid with a strong, sharp, highly irritating odor. It is a strong lachrymator (231). Chloropicrin has been used as an insecticide since 1917 and as a soil fumigant since 1920 (259). The primary use today is for preplant soil fumigation to control soil borne fungi, diseases and nematodes (231). It also is used to treat wood poles and timbers for internal decay by fungi and insects; as a warning/clearing agent for sulfuryl fluoride (structural fumigant) and methyl bromide (soil and structural fumigant); and is also used in organic synthesis. For soil fumigation and wood treatment, chloropicrin is packaged in DOT 4BW240 steel cylinders and bulk tanks which may be pressurized. When used as a warning agent for methyl bromide, chloropicrin is packaged along with the methyl bromide in steel cylinders. When used as a structural fumigation warning agent for sulfuryl fluoride, chloropicrin is packaged in small plastic bottles in DOT approved overpacks. Chloropicrin has a moderate vapor pressure (18.3 mmHg at 20 degrees C) and exists as a liquid at room temperature. Chloropicrin/methyl bromide mixtures will volatilize readily upon opening of the cylinder valve. Materials incompatible with chloropicrin are PVC, fiberglass, aluminum and magnesium and their alloys (231,260).

TOXICOLOGICAL EFFECTS

- **Acute Toxicity**: Undiluted chloropicrin is highly toxic by ingestion or direct contact with the skin or eyes. According to the American Conference of Governmental Industrial Hygienists (261), airborne

exposure to 0.3-0.37 ppm (2-2.5 mg/meters cubed) for 3-30 seconds results in eye irritation. This response is reported to be highly variable among individuals and tearing (lachrymation) may occur at airborne exposures of 0.15-0.3 ppm (1-2 mg/meters cubed) (261). Inhalation exposure to 4 ppm (26 mg/meters cubed) for a few seconds may cause some degree of incapacitation (261) and an exposure of a few seconds to 15 ppm (100 mg/meters cubed) can cause injury to the respiratory track. Exposure to concentrations above 15 ppm can result in lacrimation, vomiting, and if allowed to continue for a minute or longer, can cause pulmonary edema and possibly death (261). The American Industrial Hygiene Association Emergency Response Planning Guideline for one hour exposure to chloropicrin is 3 ppm (20 mg/meters cubed)(262). Animal studies established that the 4-hour inhalation LC50 for chloropicrin vapor in rats is 11.9 ppm (79.7 mg/meters cubed)(293) and the respiratory irritation potential threshold (RD50) in mice is 7.98 ppm (53.5 mg/meters cubed)(293). The FIFRA Toxicity Classification for chloropicrin acute effects is Category I and the signal word for that classification is "Danger."

- **Signs and Symptoms of Poisoning:** Undiluted chloropicrin is severely and immediately irritating to the upper respiratory tract, eyes and skin upon direct contact. Exposure to airborne concentrations of chloropicrin exceeding 0.15 ppm (1 mg/meters cubed) can cause tearing and eye irritation which is reversible upon termination of exposure. Prolonged inhalation exposures at airborne concentrations above 1 ppm may cause symptoms of respiratory system damage including irritation of the airways, shortness of breath and/or tightness in chest and difficulty in breathing. Inhalation exposure to very high levels, even if brief, can lead to pulmonary edema, unconsciousness and even death.
- **Chronic Toxicity/Subchronic Effects:** Studies with male and female CD rats and CD-1 mice exposed to chloropicrin vapor in whole body inhalation chambers at concentrations of 0.3, 1.0, or 3.0 ppm for six hours per day, five days per week for thirteen weeks (263) and male Fisher 344 rats exposed to chloropicrin (264) indicated that respiratory tissue is the target for chloropicrin inhalation toxicity. Portal-of-entry effects occurred in the upper respiratory tissue of animals inhaling chloropicrin vapor for 90 days at concentrations at or above 0.1 ppm (0.67 mg/meters cubed).
- **Reproductive Effects**: A study utilizing chloropicrin vapor administered by whole body inhalation for six hours per day, seven days per week to male and female CD rats at concentrations of 0.5, 1.0, or 1.5 ppm through two generations of animals indicated that reproduction fitness is not adversely affected by chloropicrin inhalation even at systemically toxic levels (265). The No Observable Adverse Effect Level (NOAEL) was 1.0 ppm for systemic toxicity and greater than 1.5 ppm for developmental toxicity and reproductive parameters.
- **Teratogenic Effects:** In a study with sexually mature virgin female Sprague-Dawley rats exposed by whole body inhalation to chloropicrin vapor for six hours per day for days 6-15 of gestation, there were no treatment-related fetal malformations (266). The incidence of developmental variations in the mid- and high-dose groups increased over the control group and was statistically significant in the high-dose group. The NOAEL for maternal toxicity was 0.4 ppm and the NOAEL for fetal toxicity was 1.2 ppm indicating that the developing fetus is not a target tissue for chloropicrin.The developmental toxicity of chloro-picrin in sexually mature virgin female New Zealand White SPF rabbits was evaluated by whole body exposure/inhalation to chloropicrin vapor for six hours per day for days 7-20 of gestation (267). There were no treatment related fetal malformations reported, the incidence of developmental variations in the mid- and high-dose groups was increased over the control group and was considered to be treatment related but was not dose related nor was it statistically significant. The NOAEL for maternal toxicity was 0.4 ppm and the NOAEL for fetal toxicity was 1.2 ppm indicating that the developing fetus is not a target tissue.
- **Mutagenic Effects:** Chloropicrin has been evaluated in several in vitro genetic toxicity test systems (268, 271). Bacterial cell testing for gene mutation produced some evidence of genetic toxicity in one of five tester strains in the presence of an exogenous metabolic activation system but testing in higher order cells (mammalian cells) did not confirm the potential for chloropicrin to produce gene mutation. Chloropicrin did not cause damage to mammalian cell DNA. In vitro testing of

mammalian cell chromosomes for damage (breaks, exchange figures, fragments, etc.) produced evidence suggestive of a clastogenic effect but the data were equivocal.

- **Carcinogenic Effects**: Six long-term bioassays have been performed to evaluate the potential of chloropicrin to cause chronic and/or carcinogenic effects by inhalation, oral, and gavage dosing (272, 276). Chronic toxicity was limited to inflammatory and other degenerative changes associated with chronic wound healing at the portal-of-entry and at associated tissues (i.e. rodent forestomach following life-long oral dosing). No neoplastic or tumorigenic response was produced by chloropicrin in any species tested by the three routes of exposure.
- **Organ Toxicity:** Target organs for chloropicrin toxicity include eyes, skin, respiratory tract and tissue associated with portal-of-entry into the body.
- **Fate in Mammals**: The octanol/water partition coefficient (Log10 Kow) is 2.50 at 25 degrees C indicating that chloropicrin would not be expected to bioaccumulate in mammalian cells (277).

ECOLOGICAL EFFECTS

- **Effects on Birds**: Little information is available about the effects of chloropicrin on bird life. A feeding study in chickens (278) demonstrated no adverse effects at doses as high as 100 ppm for 120 days. This was the highest dose tested.
- **Effects on Aquatic Organisms:** Chloropicrin is toxic to fish. For trout and bluegill the 96-hour LC50 was 0.0165 mg/L and 0.105 mg/L respectively (278).
- **Effects on Other Animals (Nontarget species):** When used according to label, exposure to nontarget species is unlikely. However, because of its toxicity to mammals and invertebrates, it can be assumed that chloropicrin may be harmful to many nontarget organisms.

ENVIRONMENTAL FATE

- **Breakdown of Chemical in Soil and Groundwater**: The half-life of chloropicrin in sandy loam soil was 8-24 hours (279) and 4.5 days (280) with carbon dioxide being the terminal breakdown product (280). Chloropicrin moves rapidly in soils within twelve inches of injection but may diffuse to a maximum depth of four feet in sandy soil (281). Since it is only slightly soluble in water, it will not move rapidly in aquatic environments. In an anaerobic aquatic/soil system, chloropicrin was converted to nitromethane with a half-life of 1.3 hours (282). In the absence of sunlight or microorganisms, chloropicrin does not undergo hydrolysis (283, 284). The calculated Henry's Law Constant is 2.51 x 10 to the minus 3 atm meters cubed mole-1 (285). The Koc for silt loam and agricultural sand soils was 5.29 and 93.59 respectively (289). Chloropicrin can be produced during chlorination of drinking water if nitrated organic contaminants are present (286, 287). In a sampling of 1,386 wells in California between 1984 and 1989, no chloropicrin was detected (288). In a sampling of 15,175 wells in Florida, chloropicrin was found in three wells at 0.035-0.068 Hg/L (288).
- **Breakdown of Chemical in Surface Water:** Since chloropicrin has a higher density than water (1.65 g/ml) and is only slightly soluble, it will sink to the bottom of surface water. The half-life of chloropicrin in water exposed to light was 31.1 hours with carbon dioxide, bicarbonate, chloride, nitrate and nitrite being the breakdown products (284).
- **Breakdown of Chemical in Plants**: No chloropicrin or nitromethane was detected in crops grown in soil treated with radiolabelled chloropicrin (290). Carbon dioxide, as the terminal breakdown product, was metabolized by plants and incorporated into natural plant biochemical compounds via the single carbon pool (291).
- **Breakdown of Chemical in Air:** Chloropicrin is efficiently photolyzed in the atmosphere. The half-life of chloropicrin in air exposed to simulated sunlight was 20 days (292). The photoproducts were phosgene (which will hydrolyze to carbon dioxide and hydrogen chloride), nitric oxide,

chlorine, nitrogen dioxide and dinitrogen tetroxide.

- **Analytical Methods:** The concentration of chloropicrin in air may be measured using Kitagawa direct reading gas detector tube#172 (Matheson-Kitagawa, East Rutherford, NJ). Gas chromatography methods are available to measure chloropicrin in air (283) and may utilize XAD-4 solid sorbent tubes (SKC Inc., Eighty Four, PA).

PHYSICAL PROPERTIES AND GUIDELINES

Physical Properties:

- **Appearance:** Heavy, colorless, liquid with a sharp odor
- **Chemical Names:** Trichloronitromethane; Methane,trichloronitro; Nitrotrichloro-methane, Nitrochloroform
- **CAS Number:** 76-06-2
- **Molecular Weight:**164.38
- **Water Solubility:** 1.6 g/L @ 25 degrees C
- **Solubility in Other Solvents:** Miscible in most organic solvents
- **Melting Point:** -64 degrees C
- **Vapor Pressure:** 18.3 mmHg @ 20 degrees C, 24 mmHg @ 25 degrees C
- **Partition Coefficient:** Not Available
- **Adsorption Coefficient:** Not Available

Exposure Guidelines:

- **ADI:** Not Available
- **MCL:** Not Available
- **RfD:** Not Available
- **PEL:** 0.1 ppm
- **HA:** Not Available
- **TLV:** 0.1 ppm TWA

BASIC MANUFACTURERS

Niklor Chemical Corp.
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REFERENCES:

References for the information in this PIP can be found in Reference List Number 10
